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Validation of a process model of CO_2 capture in an aqueous solvent, using an implicit molecular based treatment of the reactions

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Abstract

A model of a desorber for the recovery of aqueous monoethanolamine (MEA) solvent following the separation of carbon dioxide (CO_2) from flue gas from a fossil fuel power plant is presented. This model is derived from a previously developed absorber model, by using the same rate-based stage and physical property models. The novelty of this modeling framework lies in the integration into a rate-based process model of the state-of-the-art SAFT-VR thermodynamic model, in which the physical and chemical interactions are treated simultaneously, assuming that the chemical reactions are at equilibrium. Such an approach reduces the amount of experimental data needed to model the interactions of the solvent with CO_2. The implicit treatment of the chemical reactions in this formalism obviates the need to incorporate an enhancement factor or to use experimental data for the rate of reaction. The gPROMS software is employed to implement the desorber model and pilot plant data are used for the validation, without adjusting any model parameters. Very good predictions are obtained over a wide range of operating conditions.

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Carbon capture; desorber; SAFT; MEA; process model

1. Introduction

The emission of carbon dioxide (CO_2) into the atmosphere is generally considered to play a major role in climate change and particularly in global warming. In response to global warming, the Roadmap for 2050 set by the European Commission in 2011 suggested reducing greenhouse gas emissions in Europe by 25% by 2020 and by 80% by 2050. A short-term imperative is therefore the development of carbon

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capture systems. Fossil fuel power plants have been the focus of much carbon emission abatement effort as they are large fixed point-source emitters of CO_2. Post-combustion capture processes based on amine solvents are seen as the most promising near-term technology in terms of development and applicability, the major advantage of this technology being that it can be retrofitted to existing power plants [1].

The large energy requirements, solvent degradation, and the environmental and health impact that may result from solvent losses and solvent degradation products associated with this technology are however some of the important concerns in the deployment of this technology. The choice of solvent and operating conditions play an important role in achieving the best performance, and modelling studies can play an invaluable role in identifying the best design decisions.

A key challenge in realising the benefits of a model-based approach is the development of models that can accurately predict the behaviour of the process under different conditions and for different solvents, given the complex reaction chemistry that occurs during CO_2 absorption and the large number of ionic species present in the process.

In our current study, an advanced thermodynamic model of both the physical properties and the chemical reactions inherent in amine-based solvent is incorporated into a rate-based process model of the CO_2 desorber, following an approach deployed successfully in modelling an absorber [2]. This is a critical component of the overall absorption process, as the regeneration of the solvent is the major energetic and economic penalty. A version of the statistical associating fluid theory (SAFT) [3, 4] is employed to model the complex physico-chemical interactions between CO_2 and the solvent. The stage model and the physical property models at the core of the desorber are transferred directly from the absorber [2]. This approach is validated with pilot plant data [5]. In the next section the thermodynamic framework used is presented briefly and the process model is then described; the model is assessed by comparison with the pilot plant data in Section 3.

2. Proposed model of a CO_2 desorber

The desorber model developed in the current work is adapted from the absorber model presented in a previous paper [2]. This model can be divided in two parts: a thermodynamic model, in which the SAFT-VR formalism is used [3, 4], and a rate-based model. These two parts are presented here briefly.

2.1. Thermodynamic model

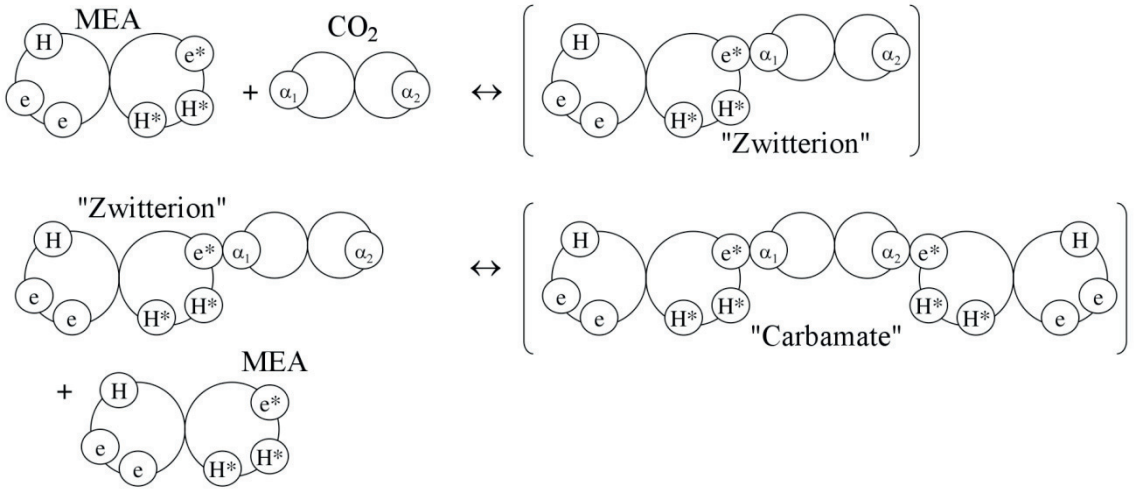
As with other SAFT approaches [6, 7, 8, 9], within the SAFT-VR equation of state [3, 4], a molecule *i* is modelled as a chain of m_i spherical attractive segments tangentially bonded to form the molecule. In our current work the segments are represented using a square-well (SW) interaction with hard-cores of diameter σ_{ii}, and the attractive interaction between two segments is described with a range λ_{ii} and well-depth ε_{ii}. The association interactions are mediated by off-centre and short range square-well association sites to describe the hydrogen bonding and complex formation characterised by site-site energetic ε_{hb} and range parameters λ_{hb}. A particular advantage of SAFT-VR is that the SW range parameter λ_{ii} can be used to account for the variable range (VR) of intermolecular interactions.

The thermodynamic properties needed to determine the fluid phase and chemical equilibrium, namely the pressure and chemical potential, are obtained as the corresponding derivatives of the Helmholtz free energy.

In a SAFT description of reacting systems such as aqueous amine solutions of CO_2 the reactions can be accounted for implicitly within the thermodynamic model, with the products of the chemical reaction treated as associated aggregates of the reactant molecules; this has been discussed at length in the context of SAFT-VR for monoethanolamine [10], alkylamines [11] and multifunction alalkanolamines [12]. By

avoiding an explicit treatment of the reactions the number of parameters needed to describe the system is reduced dramatically as only the site-site interactions between the reactant molecules need to be specified. The vapour-liquid phase equilibrium of MEA + CO_2 + H_2O can be obtained very accurately in this manner. The formation of a carbamate principal reaction of interest between CO_2 and MEA is [13]:

$$CO_2 + 2HOCH_2CH_2NH_2 \rightleftarrows [HOCH_2CH_2HCO_2^- + HOCH_2CH_2NH_3+]$$



Our implicit model of carbamate formation is presented schematically in Figure 1.

Figure 1. Schematic representation of the association scheme between MEA and CO_2in an aqueous medium (water is not shown) indicating the two key reaction products. The bonding sites α_1 and α_2 on the CO_2model mediate the formation of the zwitterion and the carbamate by bonding to the e* site (of the NH_2 group) on MEA.

The overall reaction as the generation of aggregates of the reactants can be shown to be equivalent to chemical (reaction) equilibrium [14]. An important advantage of using this approach is that it is not necessary for the reaction products (and intermediates) to be modelled explicitly, reducing the number of components required in the overall model. The concentration of carbamate in solution as a function of the CO_2 loading has been shown to be very well predicted with this approach [12].

2.2. Stage model

A two-film model is used to describe every stage of the desorber [15] (cf. the description for the absorber presented in reference [2]). A bulk phase and a film within which the chemical reaction and heat and mass transfer occur are then used to represent each phase. The concentration and temperature are assumed to be uniform in the bulk phase, while a gradient in composition and temperature may be present in the film. The pressure is taken to be uniform throughout the desorber. The two-film model is depicted in Figure 2, with the profiles for compositions, temperature and pressure.The thermodynamics of the bulk phase is modelled with SAFT-VR to determine the chemical equilibrium state, and also at the interface to determine the chemical equilibrium and phase equilibrium.

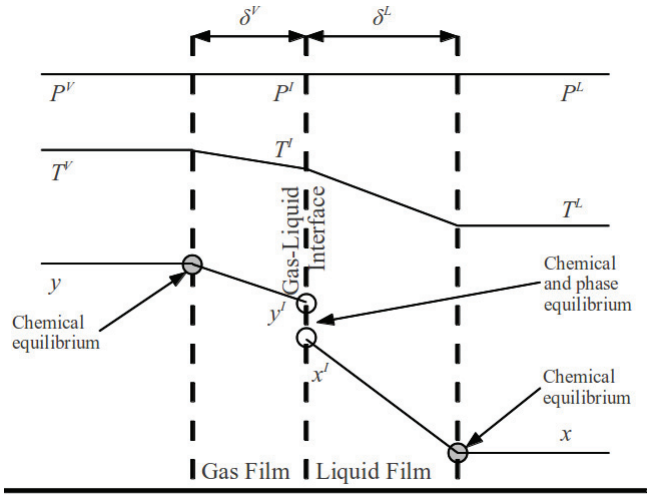


Figure 2. A schematic of the two-film model of a theoretical column stage. The thickness of the gas and liquid films are represented byδ^V and δ^L, respectively. The pressures in the bulk vapour phase, at the gas-liquid interface, and in the bulk liquid are P^V, P^I, and P^L, respectively. An isobaric profile is assumed in the current work. T^V, T^I, and T^L, denote the temperatures of the bulk gas phase, of the gas-liquid interface, and of the bulk liquid, respectively. The mole fractions in the bulk gas and liquid phases are x and y, respectively, and y^I and x^I are the corresponding mole fractions at the gas-liquid interface for the gas and the liquid phases.

2.3. Desorber model

The desorber column is divided into 50 stages, each representing a section of the packed column. A structured packing is used and so the mass transfer correlations from Rocha *et al.*[16], specifically developed for such a packing type, are implemented in the model. In the reaction-implicit model, the CO_2 in the liquid phase represents CO_2, bicarbonate and carbamate. In practice, this is mostly carbamate, a much larger species than CO_2. A scaling of the CO_2 diffusivity in the liquid phase is therefore undertaken to account for the high proportion of carbamate. The estimation of the value of the scaling factor is presented in an absorber study [2] and the value thus obtained is not modified here. In the steady-state model of the desorber we assume that:

- The fluid bulk phases and film are at chemical equilibrium at all points (i.e., the reaction rates are much faster than the mass transfer rates [13]).
- There is phase and chemical equilibrium at the interface.
- The interfacial surface area is the same for both mass and heat transfer.
- The desorption column is considered to be adiabatic.
- The pressure drop along the column is neglected.

3. Model validation

The desorber model developed in the current work is validated by comparing the model predictions with the pilot plant experimental data obtained by Tobiesen *et al.* [5]. 18 runs have been simulated out of the 19 runs presented by Tobiesen *et al.* [5]. The conditions for the final run, Run 18, have proved more challenging for our initialisation procedure and a more robust procedure is under development. The predictions for the temperature and liquid phase CO_2 loading, as calculated at the bottom of the desorber and at the reboiler outlet, are compared with the experimental values from Tobiesen *et al.*[5] for all 18

runs in Figures 3 and 4. These runs represent a wide range of operating conditions in terms of flowrate, liquid composition, heat duty, and temperature.

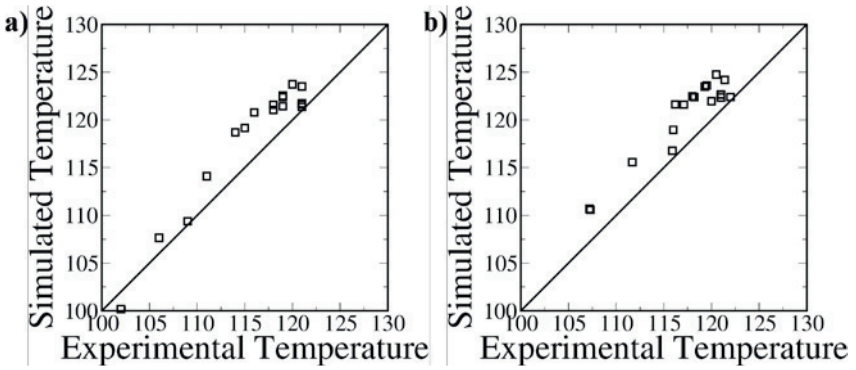


Figure 3. Experimental and simulated temperature, a) at the bottom of the desorber and b) at the reboiler outlet.

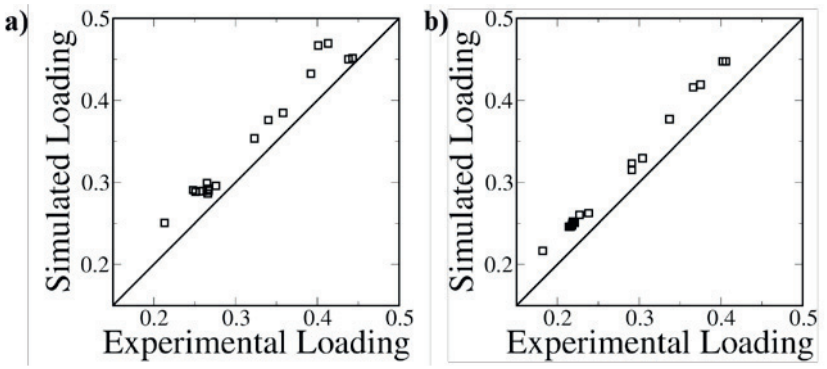


Figure 4. Experimental and simulated CO_2 loading, a) at the bottom of the desorber and b) at the reboiler outlet.

Good agreement is found between the model predictions and the pilot plant data in relation to the temperature and the loading of the desorber and the reboiler. Although there is a slight over-prediction of the CO_2 loading and the temperature in both process units, these deviations are consistent with the measurement errors described by Tobiesen *et al.* [5]. In relation to CO_2 loading, they explained that it was extremely hard to obtain sufficient accuracy in the desorber outlet loading reading. With regard to the temperature measurements, the exact position of the temperature probe at the bottom of the desorber or in the reboiler has a significant impact on the temperature reading and can lead to an error in the reboiler temperature reading of about 2-2.5K and of an even higher error in the desorber temperature reading [5].This indicates that the model developed in our current work is suitable for the operating conditions under which a CO_2 desorber operates. The model exhibits very good predictive capabilities over a wide range of operating conditions.

4. Conclusions

A rate-based CO_2desorber model incorporating a SAFT-VR thermodynamic treatment has been developed based on a previous absorber model. The desorber modelling approach is identical to our previous approach used for the absorber and therefore constitutes a good test of the predictive capabilities

of this model. The physical and chemical interactions are combined within a consistent thermodynamic framework, assuming that the chemical reactions are at equilibrium. The implicit treatment of the chemical reactions in this formalism obviates the need to incorporate an enhancement factor or to use experimental data for the rate of reaction. Such an approach greatly simplifies the description and provides a considerably more transferable model. We show that very good predictive capabilities can be obtained over a wide range of operating conditions without the need for adjusting any of the model parameters in going from the absorber to the desorber.

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